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The main aim of this work is to improve the understanding of the mechanisms of adhesion of organosilanes on metal surfaces for the design of improved adhesion promoters/primers. Our approach is to conduct molecular simulations to determine binding energies of the various molecular structures and the influence of surface contaminants, on the interaction of organosilanes with metal oxides. The initial problems have been overcome and good progress has been made in the last few months.

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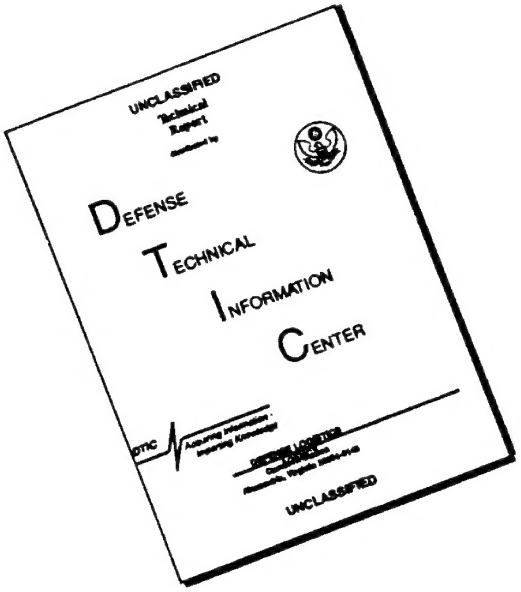

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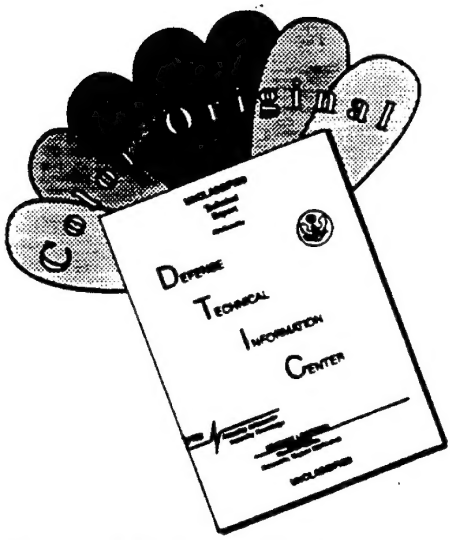

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1. Introduction

Recently, experimental work has been performed in the Department of Mechanical Engineering at Imperial College of Science, Technology and Medicine by N.G. Cave and A.J. Kinloch[1] investigating the use of self-assembling monolayer silane films as adhesion promoters. This was followed up by computational work of M.S. Sennett et al.[2] and S.A. Ojo[3], examining the interaction of hydrolysed γ-glcidoxypropyl-trimethoxysilane (GPMS) and nine variants on four metal oxide surfaces. We have continued on from this work, and attempted to use computer modelling methods developed in references two and three, to reproduce the experimental results in reference one.

2. Aims and Background

The aim of this work is to improve the understanding of the molecular level mechanism of adhesion of organosilanes on metal surfaces for the design of improved adhesion promoters/primers. Our approach has been to carry out molecular simulations to determine binding energies, molecular structure and the influence of surface contaminants on organosilane interaction with metal oxides. We have been using a variety of computer simulation methods incorporated in the Cerius[2] software package[4]. These were discussed previously[5]. We have attempted to correlate the models with experimental data, where available, in order to validate the model.

The methods we are using are based around molecular mechanics. A series of empirical forcefield terms are used to describe a system. Each of these terms is parameterised for combinations of atoms in the system we are interested in. Molecular mechanics can give excellent results, with the proper parameterisation, and is much faster than quantum mechanical methods.

We are currently using two approaches:- dynamics and sorption calculations. Each approach uses the same molecular mechanics forcefield. Our forcefield is a derivation of the Drieding Forcefield, with parameters added for the particular system we are interested in. The forcefield was derived by Dr Andreas Bick at Molecular

Simulations[6]. The dynamics approach allows us to examine the interaction of groups of molecules with the surface, and each other, over a period of time. Our sorption calculations are used to show the locations and energies available for an individual molecule with respect to the surface.

Currently, our approach to dynamics simulations is to take a silane molecule, place it in a unit cell, and minimise the cell. The cell is then repeated a number of times - usually into three by three grid, containing nine molecules. This grid of nine unit cells is then superlatticed to one unit cell, and minimised again. The density of the unit cell is compared to the published data for the silane, to ensure the cell is valid. A surface is made with the same dimensions as the silane molecules unit cell, and then the two are combined into a cell. The silane molecules are minimised above the fixed oxide surface, and then a dynamics calculation is run, for 100ps, in steps of 0.001ps, with the structure being saved every 100 steps. Once completed, the lowest energy structure is extracted from the run, and the energy of the system is evaluated. The surface is then removed, and the energy of the silane molecules is measured. Once one is taken from the other then the interaction energy is known. This energy is divided by the area of the surface, and the resulting number is converted to units of dynes/cm. This gives the work of adhesion, which can then be used to calculate the surface free energy. Other factors, such as the changes in the internal molecule bond lengths, and the surface to silane primer distances are also measured, along with examining the conformation of a silane molecule with respect to the surface and other silane molecules.

3. Modelling Studies

Initial work has concentrated on modelling basic straight chain alcohols from propan-1-ol to dodecan-1-ol, adsorbing onto aluminium oxide (corundum). This is to enable the validation of a forcefield developed by Andreas Bick at Biosym/MSI[6], with respect to the hydrogen bonding that is expected. We then proceeded to examine the fully hydrolysed silanes, with a single molecule on a surface, then we progressed to groups of such molecules on the aluminium oxide surface.

3.1 Single molecule calculations

3.1.1 Alcohols

Each of the un-branched, straight chain, primary alcohols from ethanol to dodecan-1-ol were placed above a corundum surface, and minimised. After minimisation, each had a dynamics calculation performed on it, and the lowest energy structure was extracted and minimised. The interaction energy was taken to be the difference in energy between the molecule on the surface (Total Energy), and the molecule in free space (Energy of Sole Molecule). The closest contacts were also measured between the surface oxygen and the alcohol's hydroxyl hydrogen, and the surface aluminium and the alcohol's oxygen. These values can be seen in the table below.

Table 3.1 Table of Measured Alcohol Interaction Energies And Distances - All energies are given with units of Kcal mol^{-1}.

No. of Carbons	Total Energy	Energy of Sole Molecule	Interaction Energy	$O_{surface}$-$H_{alcohol}$ Bond Length / Å	$Al_{surface}$-$O_{alcohol}$ Bond Length / Å
2	-12.03	0.28	-12.30	2.55	3.00
3	-10.18	7.58	-17.76	2.50	2.91
4	-17.85	5.43	-23.28	2.33	3.03
5	-17.51	6.13	-23.635	2.46	3.02
6	-18.28	6.93	-25.21	2.41	3.06
7	-23.37	7.69	-31.05	2.32	3.00
8	-24.24	7.97	-32.21	2.32	2.98
9	-25.19	11.77	-36.96	2.27	3.01
10	-19.16	13.55	-32.69	2.31	3.05
11	-24.50	10.61	-35.11	2.54	2.94
12	-20.86	17.03	-37.88	2.63	3.00
13	-32.58	13.87	-46.45	2.68	2.97
14	-28.64	16.05	-44.69	2.55	2.97
15	-31.59	17.89	-49.48	2.25	2.96
16	-33.06	19.42	-52.47	2.34	3.01
17	-31.55	22.33	-53.88	2.60	2.97
18	-29.27	26.22	-55.49	2.45	2.82
19	-34.19	26.81	-61.00	2.54	2.89
20	-32.59	18.07	-50.66	2.36	2.95

As can be seen, the interaction energy for the different alcohols does not greatly vary. This was to be expected, as the point of interaction is the same on each molecule (i.e.

the -OH group interacting with the oxide), and the length of the carbon chain in this case should not greatly affect the interaction energy. Closest contacts for the oxygen-hydrogen bond were all in the range of 2.25Å to 2.68Å, which is around the length expected for hydrogen bonding. Surface aluminium to alcohol oxygen values were between 3.03Å and 2.82Å, and again are in agreement with expected values.

3.1.2 Silanes

The same method was performed on a range of silane molecules from fully hydrolysed γ-glcidoxyethyltrimethoxysilane to γ-glcidoxydodecaltrimethoxysilane adsorbing onto aluminium oxide (corundum). The results were calculated as before. The table below shows the length of the carbon chain, the calculated interaction energy, and the measured bond lengths. The frame number refers to the number of the selected frame from the dynamics run, in which 1000 frames were saved. The frame was selected on the basis of representing the lowest energy observed.

Table 3.2 Table of Measured Silane Interaction Energies And Distances.

No. of Carbons	Frame no	Interaction Energy / kcal mol^{-1}	$O_{surface}$-H_{silane} Bond Length / Å	$Al_{surface}$-O_{silane} Bond Length / Å
2	310	-1.27	2.97	2.64
3	438	10.73	3.52	2.53
4	572	7.68	2.91	2.37
5	877	14.03	3.04	2.62
6	314	16.74	2.76	2.36
7	922	18.97	2.98	2.75
8	450	23.55	2.71	2.32
9	776	26.80	2.92	2.07
10	-	-	-	-
11	752	38.44	2.87	2.66
12	551	43.61	3.49	2.59
13	988	44.19	4.63	2.47
14	645	47.97	3.83	2.47
15	831	52.67	3.66	2.45
16	396	56.37	2.86	2.41
17	796	67.66	2.87	2.63
18	882	67.90	2.73	2.71
19	846	72.27	2.66	2.53
20	959	79.44	3.39	2.57

The closest contacts between the surface aluminium and silane oxygen were measured, as well as surface oxygen and silane hydrogen close contacts. Values were found to be in the range expected for this type of bonding. Our hydrogen bonding values showed a larger range than for the alcohols, and ranged from 2.07Å to 2.75Å. This larger range can be explained by the differences in the interactions. The primary alcohols had only one point of contact, whereas our silane has three hydroxyl groups, thus the molecule has more confirmations in which is can place itself on the surface, and we may not have found the closest contact in each case. The silane oxygen-surface aluminium range was also greater - 4.63Å to 2.66Å, due to the same reason. As for the alcohols, these results for a single silane molecule suggest that the interaction energy is not greatly dependent upon the length of the hydrocarbon chain. The steady increase in the interaction energy is due to the molecule not standing up at 90° to the surface, but bending over and thus allowing further interactions with the hydrocarbon chain.

3.2 Calculations for a cluster of molecules

The method used for our calculations with many molecules was based on discussions with Dr David Porter[7] who uses a similar technique for modelling interactions between liquids. A silane molecule was placed in a single unit cell on its own, and the cell and contents were minimised. Once minimisation was complete, the unit cell was multiplied into a *"three by three"* molecule box, containing nine molecules. These nine unit cells were then joined together into a superlattice, to make a new unit cell, that was once again minimised. The density was measured at various points through the minimisation process, using the density measurements controls in Cerius[2]. The calculated value was then compared to the experimentally measured value from the data sheet, and once they were in close agreement, the structure was taken to be correct. This structure was then placed above the corundum surface, and a dynamics calculation was performed. Once completed, the lowest energy structure was extracted from the saved run, and the energy measured. The surface was then removed, and the energy measured again. This difference in energy is the interaction energy. This interaction energy was then divided by the area of the surface, to give a work of adhesion.

$$\text{Work of Adhesion} = \frac{\text{Interaction Energy}}{\text{Surface Aera}}$$

As a secondary check on the silane structure, the solubility parameter was also calculated, using:

$$\delta^2 = \frac{\Delta H - RT}{M/D}$$

where δ = Solubility Parameter

ΔH = Interaction Energy between Molecules

R = Gas Constant

T = Temperature

M = Molecular Weight

D = Density

Table 3.3 Table showing calculation of solubility parameters

	GPMS	GDMS	GDDMS
ΔH /kcal mol^{-1}	1382.26	1124.86	952.057
R / J mol^{-1}K^{-1}	8.31441	8.31441	8.31441
T / K	298	298	298
M	1874.592	2758.293	4020.723
D / g cm^{-1}	1.065	0.582	0.610
δ / (cal/cc)^{½}	8.86	4.87	4.13

GPMS: hydrolysed version of γ-glcidoxypropyltrimethoxysilane

GDMS: hydrolysed version of γ-glcidoxydecaltrimethoxysilane

GDDMS: hydrolysed version of γ-glcidoxydodecaltrimethoxysilane

Literature values for GPMS are given as 9.2(cal/cc)^{½}, while data is not available for the other two structures.

3.2.1 γ-glcidoxypropyltrimethoxysilane (GPMS)

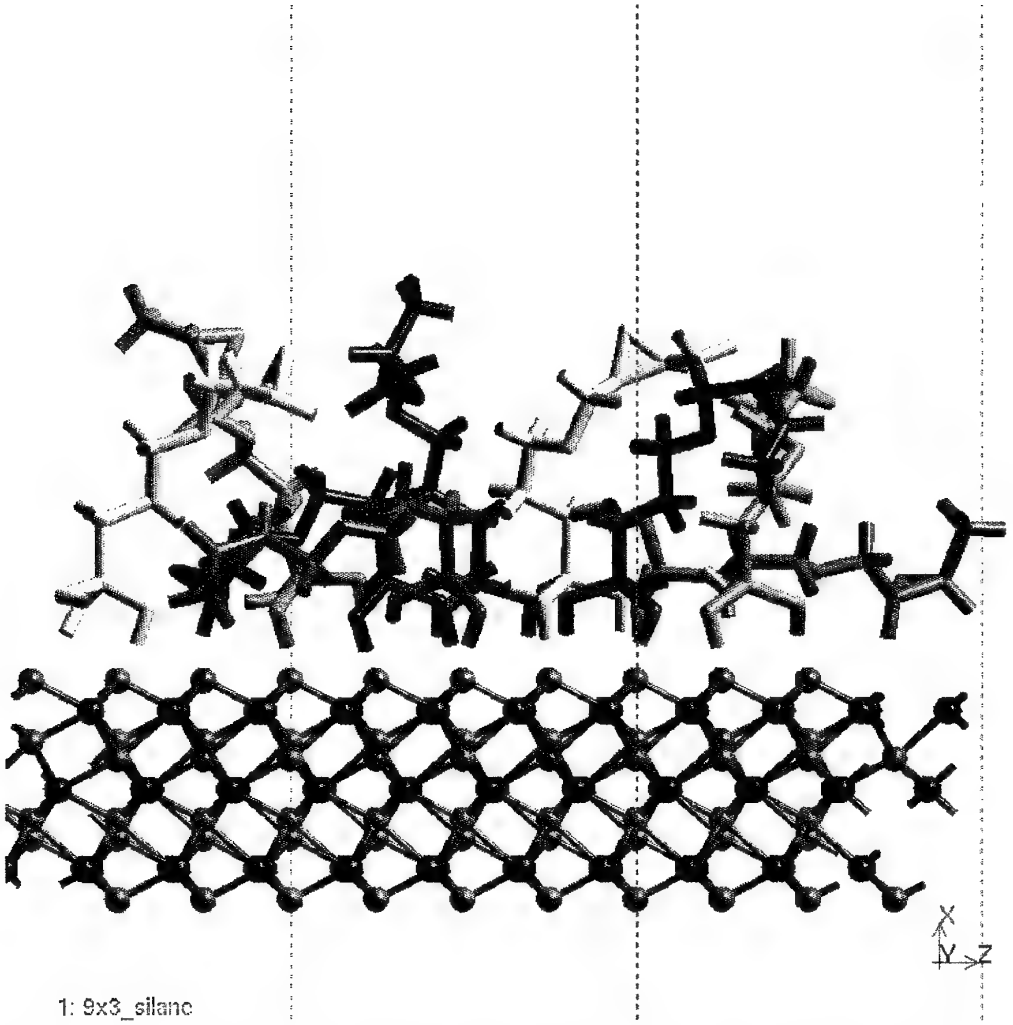
Using the method described in section 3.2, the work of adhesion was calculated as follows:

Table 3.4 Calculation of Work of adhesion for γ-glcidoxypropyltrimethoxysilane

	Total Energy	Silane Energy	Interaction Energy
I.E. / kcal mol^{-1}	-449.96	-47.96	- 402.00
I.E. / J mol^{-1}	-1,883,555.06	-200,762.96	-1,682,792.10
	X Direction / Å	Y Direction / Å	Total / $Å^2$
Area	19.00	19.00	361
	J mol^{-1} $Å^{-2}$	J m^{-2}	dyne cm^{-1}
Work of adhesion	4,661.47	0.774	774.07

The lowest energy structure extracted from the dynamics simulation is shown below. Each molecule has been coloured differently, to show the differences in position. As can be seen, some of the molecules are pointing away from the surface, and others have curved back down to lie on the surface.

Figure 3.1 Diagram of GPMS molecules on corundum surface



The changes in bond lengths were measured for the silane part of GPMS. The results are shown in Table 3.5 where the carbon-silicon bond is given first, followed by the bond lengths for each of the three Si-O-H bonds. These three pairs of bonds are equivalent. The percentage change (a small change in bond length) of the combination of all the Si-O-H bond lengths is also given. All values are given in Å. At the bottom of the table, the average for each column is given, along with the total average percentage change for each of the three types of bonds.

Table 3.5 Table of bond lengths for γ-glcidoxypropyltrimethoxysilane

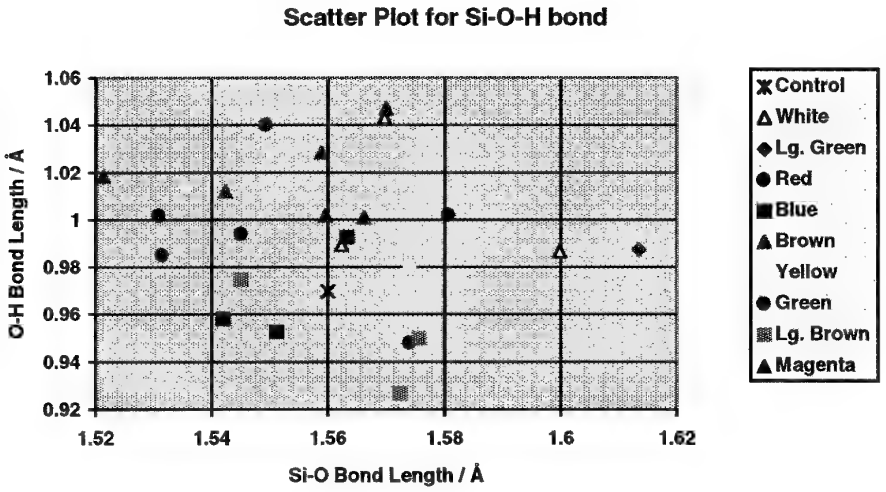
molecule	C-Si	Si-O	O-H	Si-O	O-H	Si-O	O-H	%
control	1.68	1.56	0.97	1.56	0.97	1.56	0.97	-
white	1.71	1.57	1.04	1.56	0.99	1.60	0.99	0.02%
lg. green	1.68	1.61	0.99	1.52	1.04	1.57	0.99	0.02%
red	1.73	1.58	1.00	1.55	0.99	1.53	1.00	0.01%
blue	1.69	1.55	0.95	1.56	0.99	1.54	0.96	-0.01%
brown	1.70	1.52	1.02	1.54	1.01	1.56	1.03	0.01%
yellow	1.70	1.57	0.98	1.54	1.01	1.58	0.95	0.01%
green	1.65	1.53	0.99	1.55	1.04	1.57	0.95	0.01%
lg. brown	1.69	1.58	0.95	1.55	0.97	1.57	0.93	-0.01%
magenta	1.70	1.57	1.05	1.57	1.00	1.56	1.00	0.02%
Average	1.69	1.56	1.00	1.55	1.00	1.56	0.98	
Average	0.01%	0.00%	0.02%					

Note: 1. '%' column is for the combination of all the Si-O-H bonds.

2. The 'control' molecule is the non-bonded silane in free space.

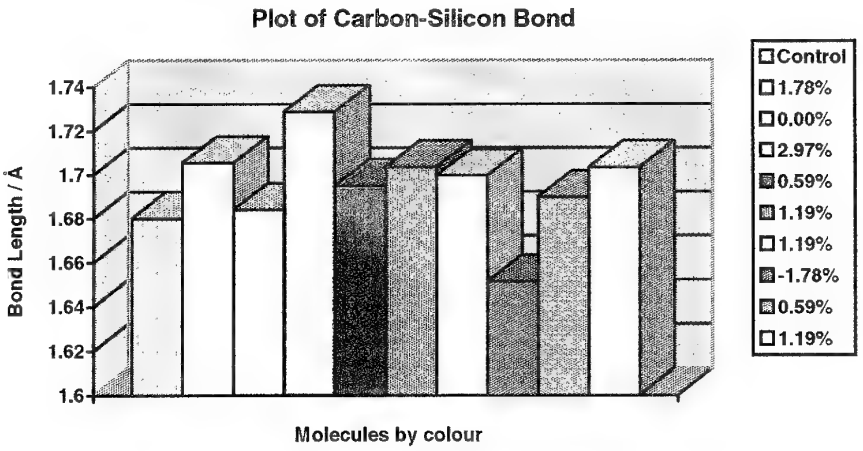
Using the data in the above table, a scatter plot has been created below (see Figure 3.2) showing the scattering of the bond lengths compared to the original molecule.

Figure 3.2 Scatter plot of Bond lengths



The percentage change in the silicon-carbon bond is shown below. It is interesting to note that the molecules which are lying on the surface - magenta, blue and red, do not show any great deviation compared to the other values.

Figure 3.3 Change in Carbon Silicon Bond Length



Measurements were made for the closest contacts between surface and silane in order to see if bonding is likely to take place. As can been seen below in Figure 3.4, the closest contact for surface aluminium and silane oxygen are around 2.47Å to 2.63Å. Whilst the surface oxygen-silane hydrogen closest contacts start at 2.04Å, in Figure 3.5.

Figure 3.4 Distance of surface aluminium and silane oxygen interactions

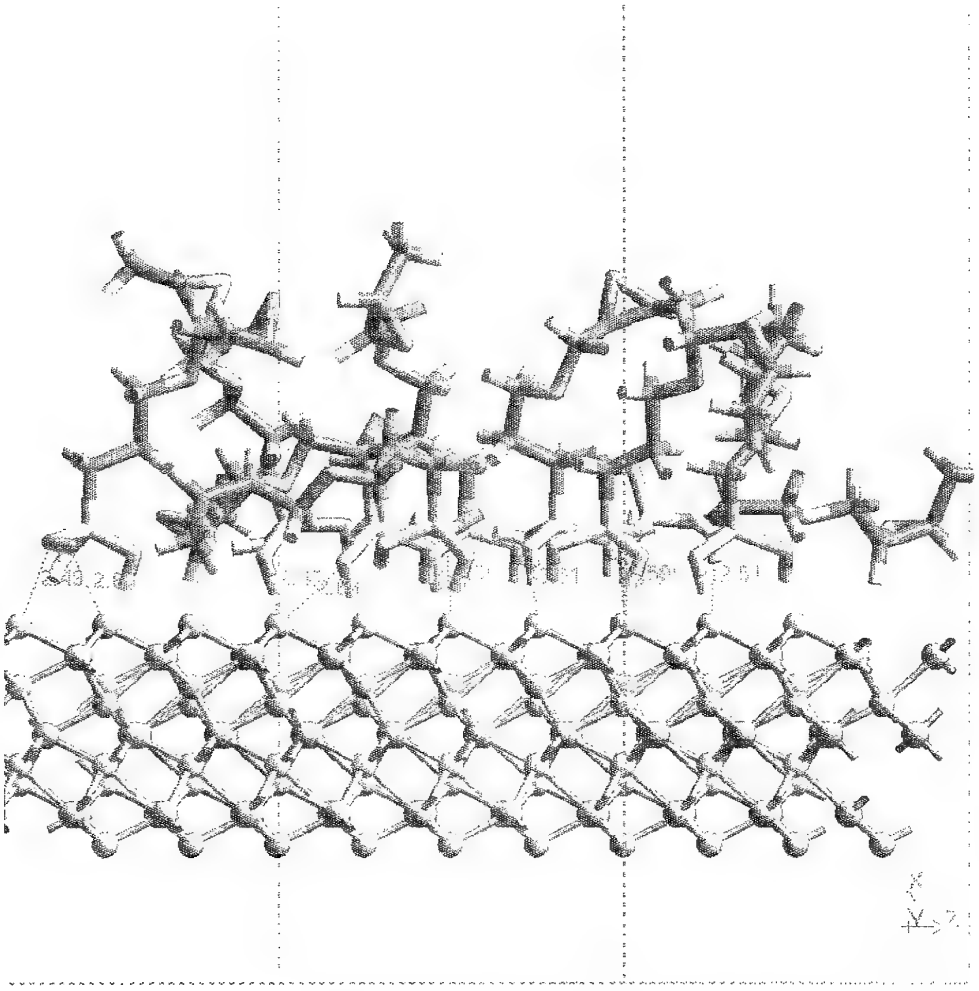
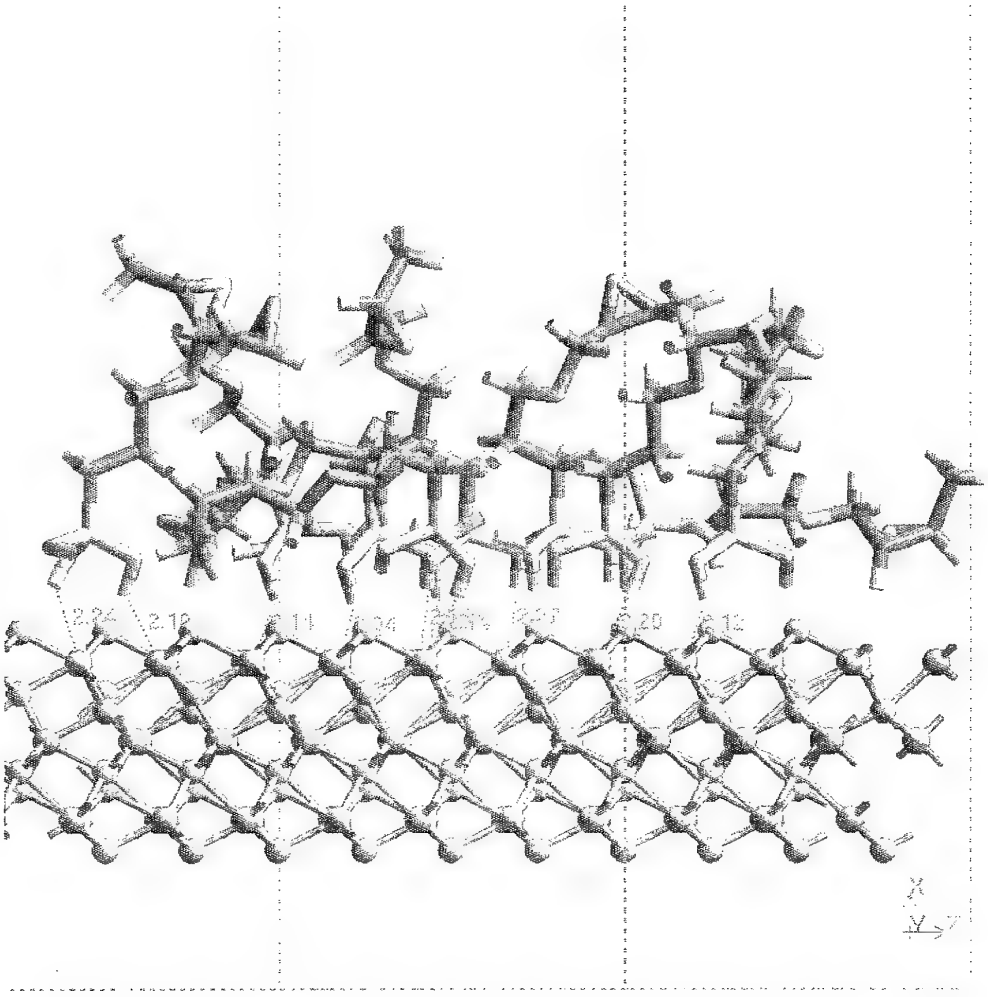


Figure 3.5 Distance of surface oxygen and silane hydrogen interactions



3.2.2 γ-glcidoxydecaltrimethoxysilane (GDMS)

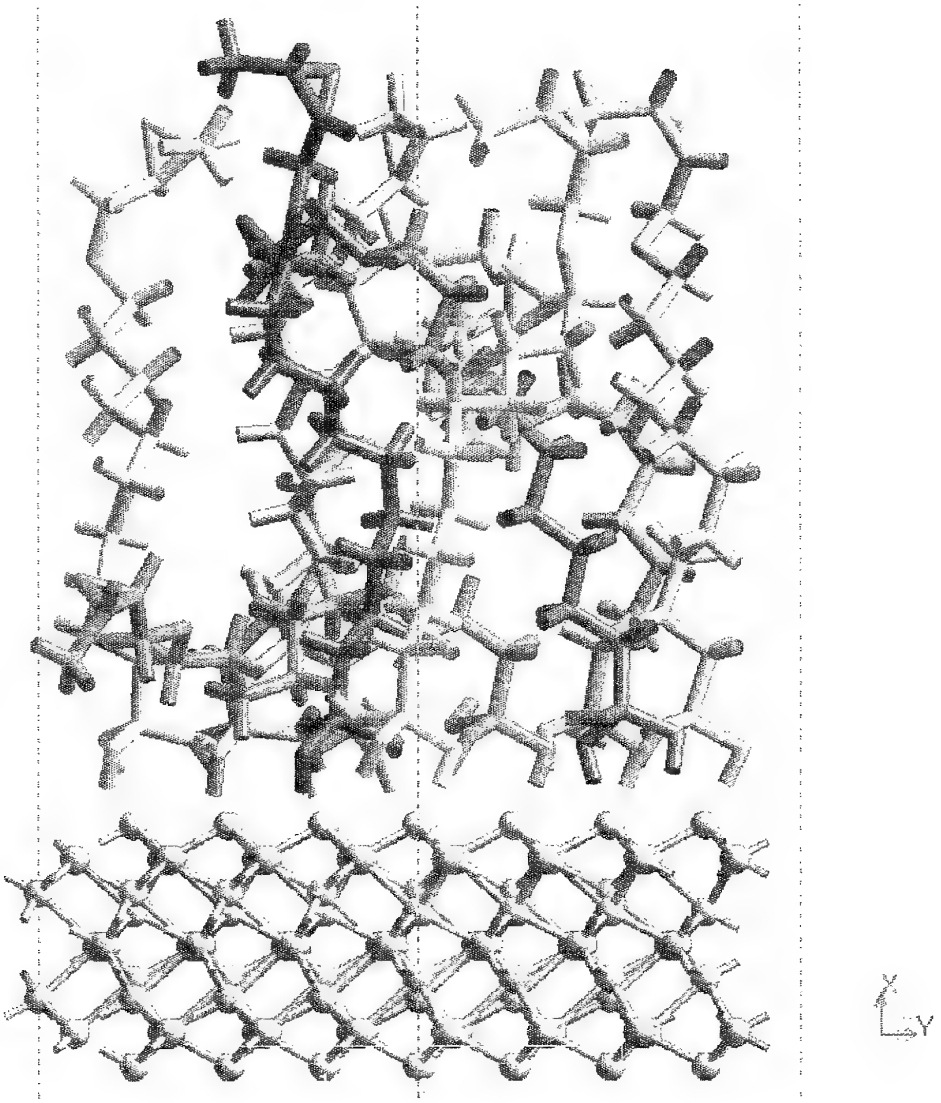
The work of adhesion was calculated as follows:

Table 3.6 Calculation of work of adhesion for γ-glcidoxydecaltrimethoxysilane

	Total Energy	Silane Energy	Interaction Energy
I.E. / kcal mol^{-1}	-328.303	37.3293	-365.6323
I.E. / J mol^{-1}	-1,374,292.77	156,262.32	-1,530,555.09
	X Direction / Å	Y Direction / Å	Total / $Å^2$
Area	19.00	19.00	361
	J mol^{-1} $Å^{-2}$	J m^{-2}	dyne cm^{-1}
Work of adhesion	4,239.76	0.704	704.04

This value is very similar to that for GPMS, as would be expected. This is due to the interactive part of the molecule being the same, so the work of adhesion should be independent of the chain length.

Figure 3.6 Diagram of GDMS molecules on corundum surface



As previously, the lowest energy structure was extracted from the dynamics run, and each molecule was coloured separately, and the change in the silane bond lengths was measured, and is shown in the table below.

Table 3.7 Table of bond lengths for γ-glcidoxydecaltrimethoxysilane

molecule	C-Si	Si-O	O-H	Si-O	O-H	Si-O	O-H	%
control	1.68	1.56	0.97	1.56	0.97	1.56	0.97	-
white	1.70	1.53	0.96	1.54	1.03	1.50	1.01	0.00%
lg. Green	1.74	1.58	0.96	1.53	1.00	1.59	0.96	0.00%
red	1.71	1.61	0.96	1.53	0.98	1.59	1.01	0.01%
blue	1.69	1.58	1.06	1.54	0.94	1.56	1.02	0.01%
brown	1.68	1.56	1.00	1.54	1.00	1.54	0.96	0.00%
yellow	1.67	1.60	1.01	1.56	1.03	1.55	1.03	0.03%
green	1.71	1.59	1.01	1.56	1.00	1.52	0.98	0.01%
lg. Brown	1.72	1.58	0.98	1.51	1.01	1.58	0.96	0.00%
magenta	1.71	1.57	0.93	1.62	0.91	1.53	1.03	0.00%
Average	1.70	1.58	0.99	1.55	0.99	1.55	1.00	
Average	0.01%	0.00%	0.02%					

Note: 1. '%' is for the combination of all the Si-O-H bonds.

2. The 'control' molecule is the non-bonded silane in free space.

The above data was used to plot a scatter plot and bar chart, shown below. The resulting percentage change being about the same as before for the GPMS.

Figure 3.7 Scatter plot of Bond lengths

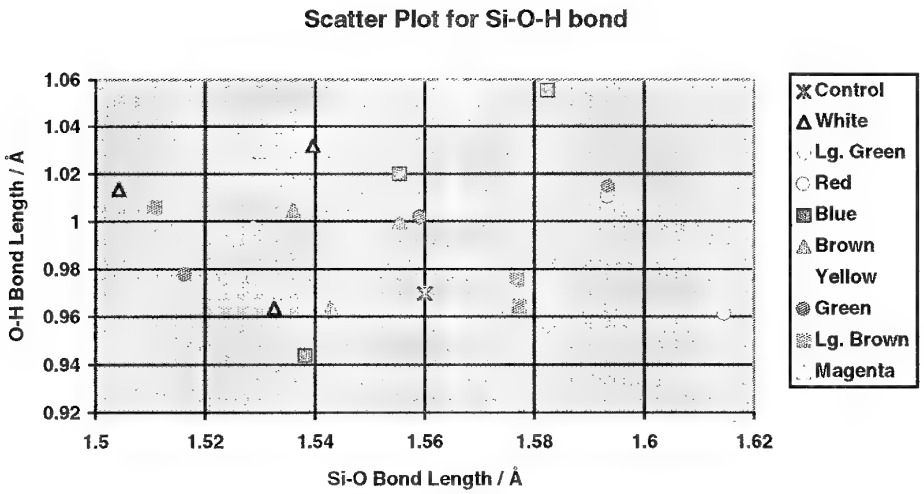
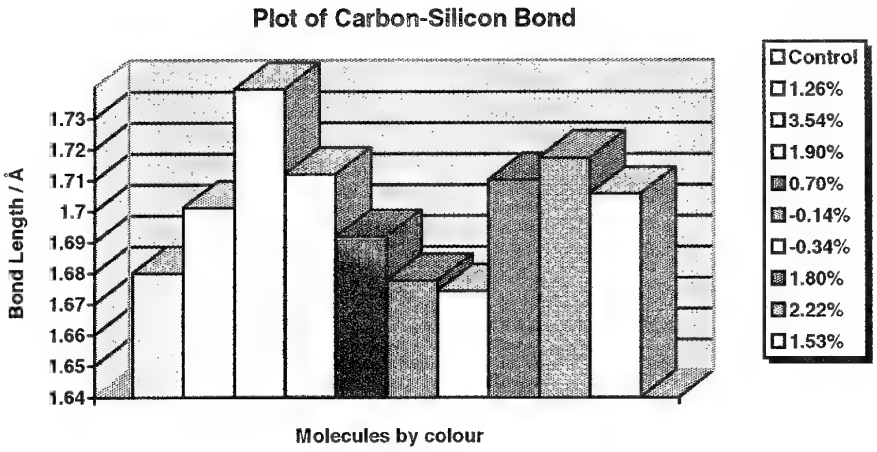


Figure 3.8 Change in Carbon Silicon Bond Length



Close contact measurements showed similar results as well, with surface aluminium to silane oxygen distances starting at 2.55Å, and surface oxygen to silane hydrogen distances starting at 1.99Å. Again these are shown below in Figure 3.9 and Figure 3.10 respectively.

Figure 3.9 Distance of surface aluminium and silane oxygen interactions

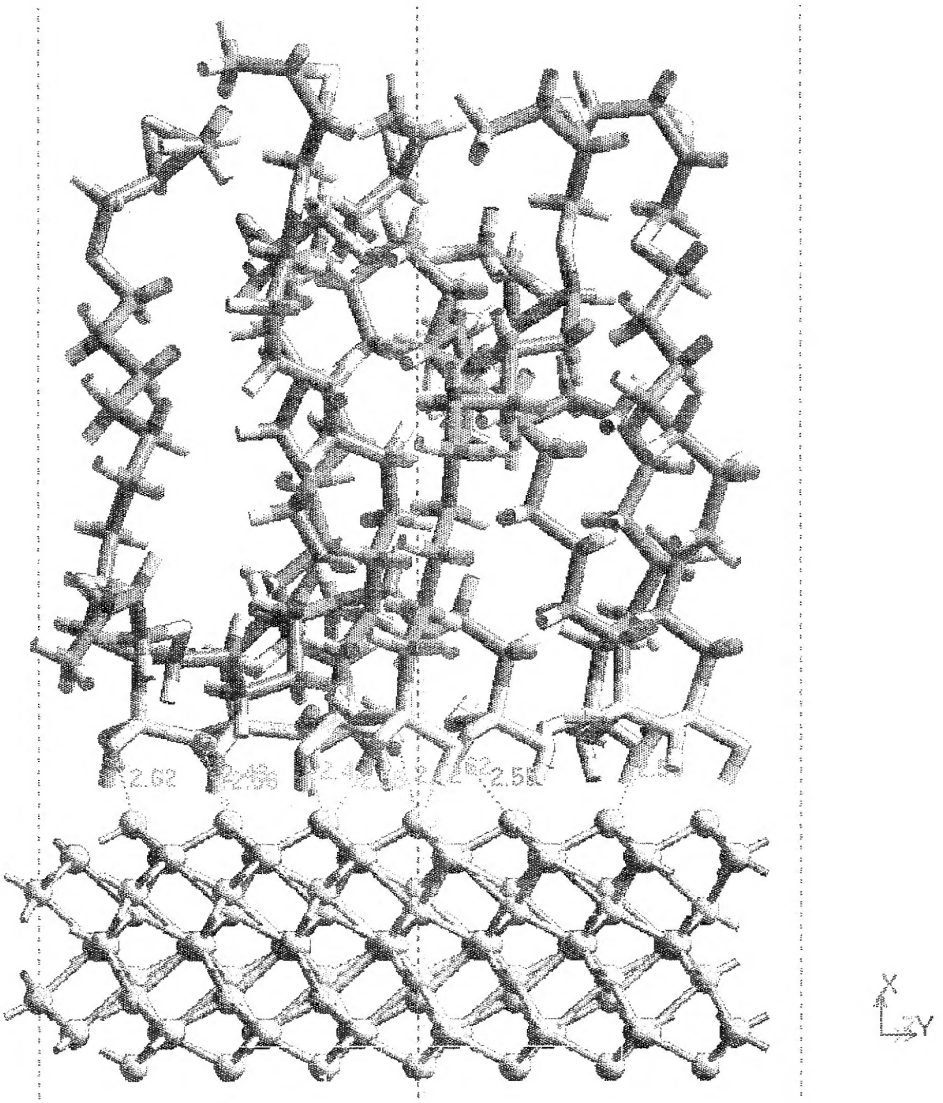
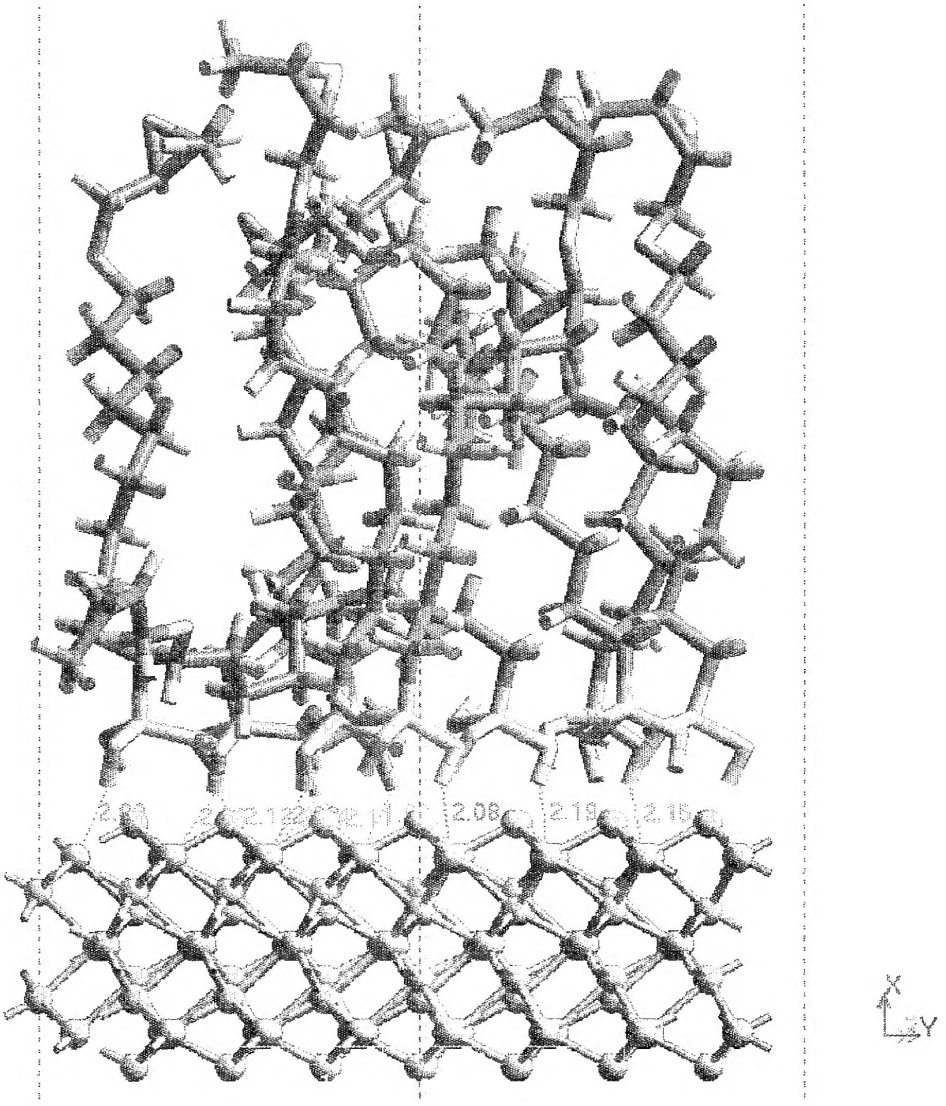


Figure 3.10 Distance of surface oxygen and silane hydrogen interactions



Increasing the carbon chain length in the silanes in this case, is having the effect of forcing the chains to stand up at right angles to the corundum surface more than in the GPMS case, compare Figure 3.5 and Figure 3.10. It is expected that the results of examining γ-glcidoxydodecaltrimethoxysilane (GDDMS), which is currently underway, will show that the chain length will force the molecules to stand up straight, as per Kinloch and Cave[1].

4. Conclusions

The distances and structures we have calculated thus far appear to give good results. . Our results give values that are in the ranges expected for this type of structure, and trends are as predicted. Molecular modelling can not obtain exact energies that can be comparable directly to experimental data, but the results can be expected to give important and valuable data trends. For example, the work of adhesion (ω_A) can be compared to the measured surface free energies (γ) using the formula:

$$\omega_A \sim 2\left(\gamma_{silane}\gamma_{Al_2O_3}\right)^{1/2}$$

Using this formula, the work of adhesion is calculated to be in the range of 350 to 500 mJ m^{-2}. The earlier calculated values, for work of adhesion, were 704 and 744 mJ m^{-2}, for the GPMS and GDMS respectively. So our values are in a similar range to those calculated using the surface free energies.

5. Future Work

1. Complete similar calculations on γ-glcidoxydodecaltrimethoxysilane (GDDMS) - this was not quite complete when this report was finished.
2. We are currently starting to run similar calculations using haematite and amorphous alumina as the surface structures, with promising results.
3. Once we have validated the forcefield against experimental values, then we will increase the complexity of our calculations to include water molecules.
4. Once successful, we will then go on to develop suggestions of new, improved primer types, based on our findings.

6. References

[1] N.G Cave and A.J. Kinloch, *Polymer*, 1992, **32**, 1162-1170.

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